

PATENT SPECIFICATION

NO DRAWINGS

1,177,545



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COMPLETE SPECIFICATION

One-Component Diazotype Material

We, KALLE AKTIENGESELLSCHAFT, a body corporate organised according to the laws of Germany, of 190—196 Rheingastrasse, Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

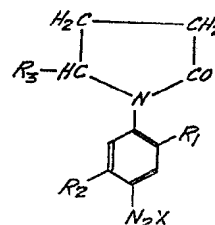
This invention is concerned with a one-component diazotype material which is suitable for the preparation of photoprints by the semi-wet process.

Diazonium compounds which are derived from unilaterally diazotized *p*-phenylene diamines which may or may not be substituted in the benzene nucleus, and carry aryl, aralkyl or acyl radicals attached to the nitrogen atom in *p*-position to the diazo groups, are being commercially used as light-sensitive substances in materials suitable for processing into photoprints by the semi-wet process. Such materials are developed by means of alkaline solutions of polyhydroxy benzenes, mainly phloroglucinol. As is known, the polyhydroxy benzenes are sensitive to atmospheric oxygen in an alkaline environment, and as a consequence thereof the developer solutions deteriorate within a short time and must be replaced at short intervals.

Thus, there exists a demand for diazonium compounds which couple at such a speed that the materials prepared with these compounds yield thoroughly developed copies within a sufficiently short time even when using neutral or weakly acid developer solutions. Some groups of diazonium compounds have been suggested for this purpose, however, they possess some defects which impede their use in light-sensitive materials, such as insufficient thermal stability or low compatibility with the

additives contained in the sensitizing solutions. Furthermore, it would be of interest to produce diazonium compounds which couple rapidly under neutral conditions and yield brown to brownish-yellow colour shades. Photoprints prepared from such compounds on transparent supports are very suitable as intermediate originals.

The present invention provides one-component diazotype material comprising a support and a layer thereon containing a light-sensitive diazonium compound corresponding to the general formula:



in which:

- R₁ stands for an alkoxy group having from 1 to 5 carbon atoms,
- R₂ stands for hydrogen, chlorine or a methyl or ethyl group, or an alkoxy group having from 1 to 5 carbon atoms,
- R₃ stands for hydrogen or a methyl group, and
- X is the anion of the diazonium compound.

This material is excellently suitable for the preparation of photoprints by the semi-wet process. The anion X may be derived from any acid known for this purpose, e.g. a hydrohalic acid, tetrafluoboric acid or hexafluorophosphoric acid. The diazonium salt may also be used in known manner in the form of a double salt,

e.g. with ZnCl_2 , CdCl_2 or SnCl_4 . Preferably, the one-component material of the invention is developed by means of weakly acid, neutral or very weakly alkaline solutions. Of course, development may instead be effected in a more strongly alkaline solution, but in that case the advantage of the high coupling speed is obviously no longer of such importance.

Depending on the substituent or substituents in the benzene ring carrying the diazonium group, colour shades ranging from deep brown to violet-tinged brown are obtained, which possess excellent colouring power and thus yield photoprints having very good contrast.

It is of advantage for the commercial use of these compounds, which have not yet been described in the literature, that they are relatively easily accessible.

They may be prepared by fusing the respective primary aromatic amines with γ -lactones in the presence of zinc chloride, nitrating the pyrrolidones thus obtained, which are mostly in the form of oily products, reducing the resulting nitro compounds, and diazotizing the primary amines thus produced.

The following Examples illustrate the invention. A detailed description of the preparation of a specific compound is contained at the end of Example 1. The other compounds listed in the Table referred to below are prepared analogously.

EXAMPLE 1.

White photoprinting base paper which had been provided with a pre-coat of polyvinyl acetate and colloidal silica was coated with an aqueous solution of the following composition:

- 0.6 g of citric acid
 - 3.5 g of boric acid
 - 2.0 g of cadmium chloride double salt of the diazonium compound derived from 1 - (2 - keto - pyrrolidino)-2,5-di-n-propoxy - 4 - amino - benzene (Compound 4 of the Table) and
 - 100.0 ml of water
- and then dried.

After exposure under a master, the sensitized paper was developed with the following solution (pH 6.0):

- 2.4 g of sodium benzoate
- 2.0 g of sodium adipate
- 9.0 g of trisodium citrate
- 0.2 g of adipic acid
- 5.0 g of sodium chloride
- 0.1 g of the sodium salt of diisopropyl-naphthalene-sulphonic acid, and
- 0.35 g of phloroglucinol in
- 100.0 ml of water.

Copies with violet-brown lines on a white background were obtained.

Equally good results were obtained by using Compound 5 of the Table, i.e. the stannic chloride double salt of the diazonium compound derived from 1 - (2 - keto - pyrrolidino)-2,5-di-n-butoxy-4-amino-benzene, or Compound 2, i.e. the stannic chloride double salt of the diazo compound derived from 1 - (2-keto-pyrrolidino)2,5-dimethoxy - 4 - amino-benzene, or Compound 8, i.e. the fluoborate of the diazo compound derived from 1-(4'-methyl-2'-keto - pyrrolidino) - 2,5 - diethoxy - 4-amino-benzene.

Compound 4, i.e. the cadmium chloride double salt of the diazo compound derived from 1 - (2 - keto - pyrrolidino) - 2,5 - di-n-propoxy-4-amino-benzene, was prepared as follows:

53.5 g of 1-amino-2,5-di-n-propoxy-benzene were heated for 8 hours with 30 ml of butyrolactone and 30 g of anhydrous zinc chloride in an oil bath having an internal temperature of 165°C while stirring. The oily condensation product obtained was further processed without purification.

Yield: approximately 110 g.

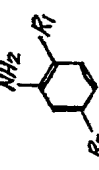
110 g of the oily condensation product thus obtained were dissolved in 500 ml of glacial acetic acid, and 33 ml of nitric acid ($d = 1.52$) were added dropwise, so that the temperature did not rise above 40°C . Subsequently, the reaction mixture was heated for a short time to 60°C , allowed to cool, and then poured into 1.5 litres of ice water. The precipitating nitro compound was drawn off by suction and thoroughly washed. For purification, it was dissolved in 500 ml of methanol, water was added until the solution became turbid and precipitation started, and the solution was then filtered over active carbon. The nitro compound thus obtained crystallized in the form of weakly yellow coloured crystals. Yield: 35.7 g. Melting point $81-83^\circ\text{C}$.

35.7 g of the resulting nitro compound were dissolved in 200 ml of methanol and reduced with Raney-nickel in an autoclave having a capacity of 0.5 litres. The reaction solution was drawn off from the nickel and evaporated under reduced pressure. In order to isolate the amine, the hydrochloride of the amino compound was precipitated by adding 10 ml of 32% hydrochloric acid. Yield: 26.8 g. Melting point: the substance begins to char at 215°C .

For diazotization of the base, 13.6 g of the hydrochloride of the amino compound were dissolved in 50 ml of water and 8 ml of approximately 32% hydrochloric acid and then 20 ml of 2N-sodium nitrite solution were added, dropwise, at a temperature of $0-5^\circ\text{C}$. The reaction mixture was filtered over active carbon and the diazo compound was precipitated by adding 5 g of sodium chloride and 1.8 g of cadmium chloride. For purification, the wet product was dissolved in 130 ml of cold water and the solution filtered and re-

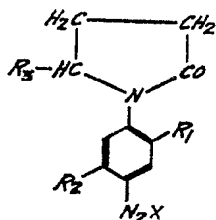
- precipitated by adding sodium chloride in an amount corresponding to 10 per cent of the diazotization solution. Yield: 15 g of yellow crystals. Melting point: 129—130° C, with decomposition.
- Compounds 5, 2 and 8 are prepared analogously to Compound 4, using the corresponding amino compounds as starting materials.
- EXAMPLE 2.**
- Pretreated white photoprinting base paper was coated as described in Example 1 with a solution which contained, in 100 ml of water:
- 0.3 g of citric acid
 - 4.0 g of the sodium salt of naphthalene-1,3,6-trisulphonic acid and
 - 1.8 g of the fluoborate of the diazo compound derived from 1 - (2 - keto-pyrrolidino) - 2,5 - dimethoxy - 4-aminobenzene (Compound 3)
- and dried. After exposure, a solution (pH 9.8) containing
- 0.4 g of trisodium citrate
 - 2.0 g of trisodium phosphate
 - 2.0 g of sodium borate
 - 0.6 g of phloroglucinol
 - 0.6 g of resorcinol and
 - 0.1 g of the sodium salt of diisopropyl-naphthalene-sulphonic acid in 100 ml of water
- was applied as a thin layer. Copies with brown lines on a white background were thus obtained.
- Compound 3 is prepared analogously to the preparation of Compound 4 described in Example 1.
- EXAMPLE 3.**
- Transparent paper was coated with a solution containing
- 0.5 g of citric acid
 - 2.5 g of the sodium salt of naphthalene-1,3,6-trisulphonic acid, and
 - 1.5 g of the fluoborate of the diazo compound derived from 1 - (2 - keto-pyrrolidino) - 2 - methoxy - 5-chloro-4-aminobenzene (Compound 1)
- in 100 ml of water and dried. For development of the exposed material, the following solution (pH 6.2) was employed:
- 8.0 g of trisodium citrate
 - 4.0 g of sodium chloride
 - 2.0 g of sodium benzoate
 - 2.0 g of sodium adipate
 - 0.15 g of citric acid
 - 0.1 g of the sodium salt of diisopropyl-naphthalene-sulfonic acid
 - 0.3 g of phloroglucinol, and
 - 100.0 ml of water
- Copies with brownish-yellow lines were obtained which were suitable as intermediate originals, for the preparation of further copies.
- Instead of Compound 1, Compound 6, i.e. the zinc chloride double salt of the diazo compound derived from 1 - (2-keto-pyrrolidino)-2 - methoxy - 5 - methyl - 4 - aminobenzene, or Compound 7, i.e. the hexafluorophosphate of the diazo compound derived from 1 - (2-keto-pyrrolidino) - 2 - methoxy - 4 - amino - benzene, may be used with equally good results.
- Compounds 1, 6 and 7 are prepared analogously to the preparation of Compound 4, with the exception that in the case of the preparation of Compound 7, nitration is effected prior to condensation with butyrolactone.
- In the following Table, the diazo compounds are of the general formula given above in which R₃ and X are as indicated in the Table. "Decomp. Pt." means "Decomposition Point".

TABLE

Compound	Starting Material 	Condensation Product with Butyrolactone	Nitro Compound	Amino Compound or Amino Hydrochloride	Diazonium Compound R_3 X Decomp. Pt. °C.
1	$R_1 = \text{methoxy}$ $R_2 = \text{chlorine}$	white, crystalline substance M.P.: 108—109°C	yellow crystalline compound M.P.: 156—158°C	Aminohydrochloride M.P.: sinters at 200°C and begins to decompose slowly	$R_3 = H$ $X = BF_4^-$ 122
2	$R_1 = \text{methoxy}$ $R_2 = \text{methoxy}$	brownish viscous oil	yellow crystalline compound M.P.: 142—145°C	Amine M.P.: 121—122°C	$R_3 = H$ $X = Cl^- \cdot SnCl_4$ 149
3	$R_1 = \text{ethoxy}$ $R_2 = \text{ethoxy}$	greenish viscous oil	pale yellow compound M.P.: 115—116°C	Aminohydrochloride M.P.: 230°C Amine M.P.: 121—122°C	$R_3 = H$ $X = Cl^- \cdot X = PF_6^-$ 124 145
4	$R_1 = n\text{-propoxy}$ $R_2 = n\text{-propoxy}$	yellow viscous oil	yellow crystalline compound M.P.: 81—83°C	Aminohydrochloride M.P.: begins to char at 215°C	$R_3 = H$ $X = Cl^- \cdot CdCl_2$ 2 129—130
5	$R_1 = n\text{-butoxy}$ $R_2 = n\text{-butoxy}$	brownish viscous oil	yellow crystalline compound M.P.: 81—82°C	Aminohydrochloride M.P.: begins to char at 210°C	$R_3 = H$ $X = Cl^- \cdot SnCl_4$ 130
6	$R_1 = \text{methoxy}$ $R_2 = \text{methyl}$	brownish viscous oil	yellow crystalline compound M.P.: 146—157°C	Amine M.P.: 137—140°C	$R_3 = H$ $X = Cl^- \cdot ZnCl_2$ 2 102
7	$R_1 = \text{methoxy}$ $R_2 = H$	—	yellow crystalline compound M.P.: 114—115°C	Aminohydrochloride	$R_3 = H$ $X = PF_6^-$ 102
8	$R_1 = \text{ethoxy}$ $R_2 = \text{ethoxy}$	yellow-brown viscous oil, after condensation with γ -methylbutyrolactone	pale yellow compound M.P.: 91—92°C	aminohydrochloride M.P.: 220°C (with decomposition)	$R_3 = CH_3$ $X = PF_6^-$ 139—140

WHAT WE CLAIM IS:—

1. One-component diazotype material comprising a support and a layer thereon containing a light-sensitive diazonium compound
 5 corresponding to the general formula:



in which:

R₁ stands for an alkoxy group having from 1 to 5 carbon atoms,

R₂ stands for hydrogen, chlorine or a methyl or ethyl group, or an alkoxy group having from 1 to 5 carbon atoms,

R₃ stands for hydrogen or a methyl group, and

X is the anion of the diazonium compound.

2. A one-component diazotype material as claimed in Claim 1, substantially as described in any one of the Examples herein.

3. A photoprint when produced by image-wise exposure and development, with a solution containing a coupling component of a material as claimed in claim 1 or 2.

4. A photoprint as claimed in claim 3, when produced substantially as described in any one of the Examples herein.

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